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(71) Applicant: Nissan Chemical Industries, Ltd.  
Chiyoda-ku, Tokyo 101-0054 (JP)

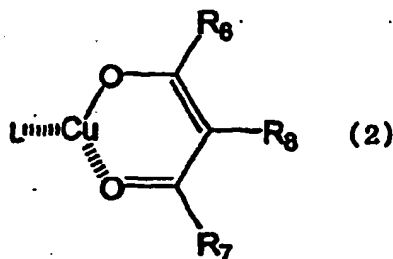
(72) Inventors:  
• **WATANABE, Hisayuki,**  
Nissan Chemical Industries Ltd  
Funabashi-shi, Chiba 274-8507 (JP)

• **MUSASHI, Hideki,**  
Nissan Chemical Industries, Ltd  
Funabashi-shi, Chiba 274-8507 (JP)  
• **KAWAMURA, Yasuo,**  
Nissan Chemical Industries, Ltd  
Funabashi-shi, Chiba 274-8507 (JP)

(74) Representative: **HOFFMANN EITL**  
**Patent- und Rechtsanwälte**  
**Arabellastrasse 4**  
**81925 München (DE)**

(54) **\$g(b)\$-DIKETONATOCOPPER(I) COMPLEX CONTAINING ALLENE COMPOUND AS LIGAND  
AND PROCESS FOR PRODUCING THE SAME**

(57) A  $\beta$ -diketonatocopper(I) complex which contains as a ligand (L) an allene compound and is represented by formula (2)



wherein,  $R_6$  and  $R_7$  may be the same or different and each represents linear or branched  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, or linear or branched  $C_{1-4}$  fluoroalkyl,  $R_8$  represents hydrogen or fluorine, and L represents the allene compound, and a process for producing the same. The complex is useful in forming a thin copper film by metal-organic vapor deposition (hereinafter abbreviated as MOCVD) method.

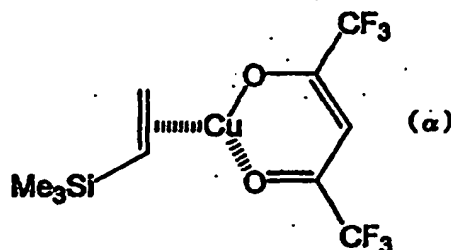
## Description

## Technical Field

- 5 [0001] The present invention relates to a  $\beta$ -diketonatocopper(I) complex useful in forming a thin copper film by metal-organic vapor deposition (hereinafter abbreviated as MOCVD) method and a process for producing the same.

## Background Art

- 10 [0002] Conventionally, as a raw material for forming a thin copper film by MOCVD method, is well known  $\beta$ -diketonatocopper(I) complex comprising (vinyltrimethylsilane) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) of formula (a)



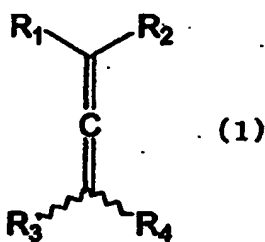
25 disclosed in Japanese Patent Laid-open No. Hei 5-59551.

[0003] However, vinyltrimethylsilane is used as a ligand for the  $\beta$ -diketonatocopper(I) complex of the formula (a). Conventionally,  $\beta$ -diketonatocopper(I) complex in which an allene compound is used as a ligand has not been known.

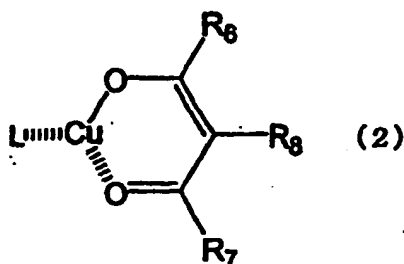
30 Disclosure of Invention

[0004] The present inventors research hard to find out novel  $\beta$ -diketonatocopper(I) complex in which an allene compound is used as a ligand from the above-mentioned viewpoint, and come to obtain  $\beta$ -diketonatocopper(I) complexes of formula (2) described below in which an allene compound of formula (1) described below is used as a ligand.

- 35 [0005] That is, the present invention relates to a  $\beta$ -diketonatocopper(I) complex which contains as a ligand (L) an allene compound of formula (1)



- 50 wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represents hydrogen,  $C_{1-4}$  alkyl or  $(R_5)_3Si-$ , or  $R_1$  and  $R_2$ , together with the carbon atom bonding them, may form 3- to 6-member ring, or  $R_2$  and  $R_3$ , together with the allene bond group bonding them, may form 8- to 10-member ring,  $R_5$ s may be the same or different and independently of one another represent linear or branched  $C_{1-4}$  alkyl, and which is represented by formula (2)
- 55



15 wherein,  $R_6$  and  $R_7$  may be the same or different and each represents linear or branched  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, or linear or branched  $C_{1-4}$  fluoroalkyl,  $R_8$  represents hydrogen or fluorine, and L represents the allene compound of formula (1).

[0006] Then, the present invention will be concretely explained.

[0007] The following is exemplified for each of the substituents in the chemical structural formula of allene compounds represented by formula (1) that is the ligand in the  $\beta$ -diketonatocopper(I) complexes of formula (2).

20 [0008] The substituents  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  include, for example H, Me, Et, n-Pr, n-Bu, i-Pr, i-Bu, s-Bu, t-Bu,  $Me_3Si$ ,  $Et_3Si$ ,  $n-Pr_3Si$ ,  $n-Bu_3Si$ ,  $i-Pr_3Si$ ,  $t-Bu_3Si$ ,  $s-Bu_3Si$ ,  $t-Bu_3Si$ ,  $Me_2(Et)Si$ ,  $Me_2(n-Pr)Si$ ,  $Me_2(n-Bu)Si$ ,  $Me_2(i-Pr)Si$ ,  $Me_2(t-Bu)Si$ ,  $Me_2(s-Bu)Si$ ,  $Me_2(t-Bu)Si$ ,  $Et_2(Me)Si$ ,  $Et_2(n-Pr)Si$ ,  $Et_2(n-Bu)Si$ ,  $Et_2(i-Pr)Si$ ,  $Et_2(t-Bu)Si$ ,  $Et_2(s-Bu)Si$ ,  $Et_2(t-Bu)Si$ ,  $n-Pr_2(Me)Si$ ,  $n-Pr_2(Et)Si$ ,  $n-Pr_2(i-Pr)Si$ ,  $n-Pr_2(n-Bu)Si$ ,  $n-Pr_2(s-Bu)Si$ ,  $n-Pr_2(t-Bu)Si$ ,  $n-Bu_2(Me)Si$ ,  $n-Bu_2(Et)Si$ ,  $n-Bu_2(n-Pr)Si$ ,  $n-Bu_2(i-Pr)Si$ ,  $n-Bu_2(t-Bu)Si$ ,  $n-Bu_2(s-Bu)Si$ ,  $n-Bu_2(t-Bu)Si$ ,  $i-Pr_2(Me)Si$ ,  $i-Pr_2(Et)Si$ ,  $i-Pr_2(n-Pr)Si$ ,  $i-Pr_2(n-Bu)Si$ ,  $i-Pr_2(s-Bu)Si$ ,  $i-Pr_2(t-Bu)Si$ ,  $i-Bu_2(Me)Si$ ,  $i-Bu_2(Et)Si$ ,  $i-Bu_2(n-Pr)Si$ ,  $i-Bu_2(n-Bu)Si$ ,  $i-Bu_2(i-Pr)Si$ ,  $i-Bu_2(s-Bu)Si$ ,  $i-Bu_2(t-Bu)Si$ ,  $s-Bu_2(Me)Si$ ,  $s-Bu_2(Et)Si$ ,  $s-Bu_2(n-Pr)Si$ ,  $s-Bu_2(n-Bu)Si$ ,  $s-Bu_2(i-Pr)Si$ ,  $s-Bu_2(t-Bu)Si$ ,  $s-Bu_2(s-Bu)Si$ ,  $t-Bu_2(Me)Si$ ,  $t-Bu_2(Et)Si$ ,  $t-Bu_2(n-Pr)Si$ ,  $t-Bu_2(n-Bu)Si$ ,  $t-Bu_2(i-Pr)Si$ ,  $t-Bu_2(t-Bu)Si$  or  $t-Bu_2(s-Bu)Si$ .

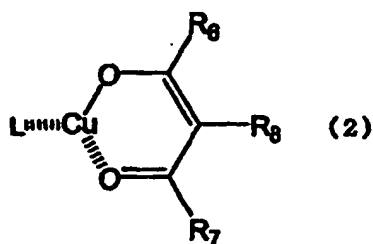
[0009] When  $R_1$  and  $R_2$ , together with the carbon atom bonding them, form 3- to 6-member ring, the ring includes cyclopropane ring, cyclobutane ring, cyclopentane ring or cyclohexane ring.

30 [0010] When  $R_2$  and  $R_3$ , together with the allene bond group bonding them, form 8- to 10-member ring, the ring includes cyclooctane ring, cyclononane ring or cyclodecane ring.

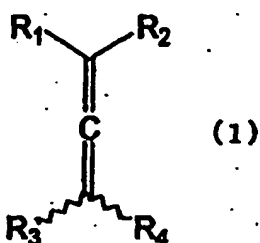
[0011] The following is exemplified for each of the substituents in the chemical structural formula of the  $\beta$ -diketonatocopper(I) complexes of formula (2).

35 [0012] The substituents  $R_6$  and  $R_7$  include, for example,  $CF_3$ ,  $C_2F_5$ ,  $n-C_3F_7$ ,  $i-C_3F_7$ ,  $n-C_4F_9$ , Me, Et, n-Pr, n-Bu, i-Pr, i-Bu, s-Bu, t-Bu, MeO, EtO, n-PrO, n-BuO, i-PrO, i-BuO, s-BuO or t-BuO. In addition, the substituent  $R_8$  includes, for example H or F.

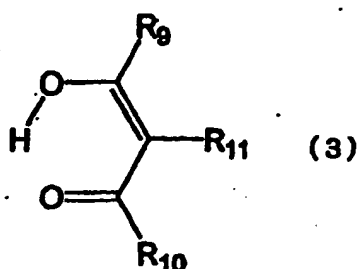
[0013] The present invention also relates to a process for producing a  $\beta$ -diketonatocopper(I) complex represented by formula (2)



50 wherein,  $R_6$  and  $R_7$  may be the same or different and each represents linear or branched  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, or linear or branched  $C_{1-4}$  fluoroalkyl,  $R_8$  represents hydrogen or fluorine, and L represents the allene compound of formula (1), characterized in that the process comprises reacting an allene compound of formula (1)

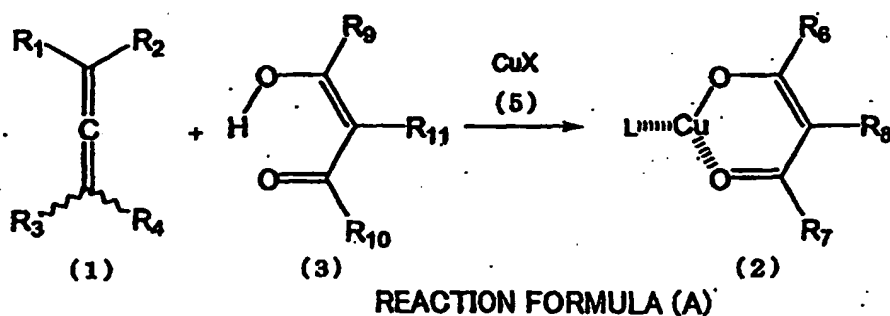


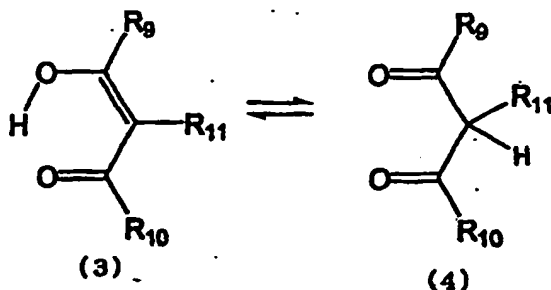
wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represents hydrogen,  $C_{1-4}$  alkyl or  $(R_5)_3Si-$ , or  $R_1$  and  $R_2$ , together with the carbon atom bonding them, may form 3- to 6-member ring, or  $R_2$  and  $R_3$ , together with the allene bond group bonding them, may form 8- to 10-member ring,  $R_5$ s may be the same or different and independently of one another represent linear or branched  $C_{1-4}$  alkyl, with an enol compound of formula (3)



wherein  $R_9$  and  $R_{10}$  may be the same or different and each represents linear or branched  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, or linear or branched  $C_{1-4}$  fluoroalkyl,  $R_{11}$  represents hydrogen or fluorine in the presence of a copper(I) compound.

[0014] Next, the process for producing a  $\beta$ -diketonatocopper(I) complex according to the present invention will be explained in more detail on the basis of reaction formulae (A) and (B).





REACTION FORMULA (B)

in formula (1) in reaction formula (A),  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represents hydrogen,  $C_{1-4}$  alkyl or  $(R_5)_3Si-$ , or  $R_1$  and  $R_2$ , together with the carbon atom bonding them, may form 3- to 6-member ring, or  $R_2$  and  $R_3$ , together with the allene bond group bonding them, may form 8- to 10-member ring,  $R_5$ s may be the same or different and independently of one another represent linear or branched  $C_{1-4}$  alkyl,

in formula (3) or (4),  $R_9$  and  $R_{10}$  may be the same or different and each represents linear or branched  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, or linear or branched  $C_{1-4}$  fluoroalkyl,  $R_{11}$  represents hydrogen or fluorine,

in formula (2),  $R_6$  and  $R_7$  may be the same or different and each represents linear or branched  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, or linear or branched  $C_{1-4}$  fluoroalkyl,  $R_8$  represents hydrogen or fluorine, and L represents the allene compound of formula (1).

[0015] In the reaction represented by reaction formula (A), a  $\beta$ -diketonatocopper(I) complex in which an allene compound is coordinated can be synthesized by reacting an allene compound of formula (1) with an enol compound of formula (3) or a carbonyl compound of formula (4) (the compound of formula (4) is a tautomer of the compound of formula (3)) together with a copper(I) compound ( $CuX$ ) of formula (5) optionally in the presence of a base (for example, inorganic base, such as sodium hydride, potassium hydride, sodium amide, potassium tertiary butoxide, potassium carbonate or the like).

[0016] The copper(I) compound includes, for example,  $Cu_2O$ ,  $CuF$ ,  $CuCl$ ,  $CuBr$ ,  $CuI$ ,  $CuOAc$ ,  $CuCN$ ,  $CuSCN$ ,  $CuOTf$  and so on.

[0017] The enol compound of formula (3) is a tautomer of the carbonyl compound of formula (4) as indicated in reaction formula (B).

[0018] The molar ratio of the allene compound to the enol compound may be arbitrarily set. However, it is preferable that the enol compound and allene compound are mixed in an amount equimolar or close thereto. For example, the molar ratio of the enol compound to the allene compound may be 0.5 to 1.5.

[0019] The molar ratio of the allene compound to the copper(I) compound may be arbitrarily set. However, it is preferable that copper atoms in the copper(I) compound are equimolar with allene compound or that an excessive of the copper atoms is mixed with the allene compound. For example, the molar ratio of the copper atoms to the allene compound may be 0.5 to 3. The molar ratio of the base to the allene compound may be arbitrarily set. However, it is preferable that the base is equimolar with the allene compound or that an excessive of the base is mixed with the allene compound. For example, the molar ratio of the base to the allene compound may be 0.5 to 3.

[0020] Although the reaction temperature is not particularly limited, the reaction may be carried out generally at a temperature between  $-110^\circ C$  and a boiling point of the solvent used in the reaction.

[0021] It is preferable to use solvents that do not participate in the reaction. The solvents that can be used include hydrocarbons (such as, hexane, pentane, benzene, toluene or the like), ethers (such as, diethyl ether, monoglyme, isopropyl ether, tetrahydrofuran, 1,4-dioxane or the like) and halogenated hydrocarbons (such as, dichloromethane, chloroform, dichloroethane or the like).

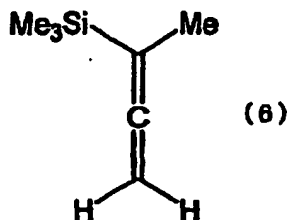
[0022] The  $\beta$ -diketonatocopper(I) complex according to the present invention is useful as a compound for forming a thin copper film by MOCVD method.

#### Best Mode for carrying out the Invention

[0023] The present invention will be concretely described on the basis of the following examples, but the present invention is not limited thereto at all.

## (Example 1)

[0024] Under nitrogen atmosphere, into 3.0 g of copper(I) oxide was poured 30 ml of dry dichloromethane that was fully degassed and the atmosphere of which was replaced with nitrogen to give a suspension solution. 1.77 g of 1-methyl-1-(trimethylsilyl) allene was added to the solution with vigorous stirring, then 3.2 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was slowly added from a dropping funnel. After the reaction solution was stirred for 12 hours, the solution was filtered under nitrogen atmosphere, and the filtrate was concentrated under reduced pressure at room temperature to give a green liquid. The liquid was purified through a column chromatography to give 4.2 g of [1-methyl-1-(trimethylsilyl) allene] (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1-methyl-1-(trimethylsilyl) allene as a ligand represented by formula (6)



as an yellow liquid.

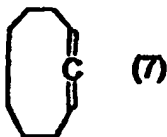
[0025] The resulting  $\beta$ -diketonatocopper(I) complex was identified with  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ .  $^1\text{H-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ) 0.19 (s, 9H), 1.97-1.99 (m, 3H), 4.14-4.16 (m, 2H), 6.15 (s, 1H).  $^{13}\text{C-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ) -2.29 (3C), 17.09, 51.00, 90.21, 96.13, 117.69 (q,  $J_{\text{C-F}}=283.7\text{Hz}$ , 2C), 173.87, 178.33 (q,  $J_{\text{C-CF}}=34.5\text{Hz}$ , 2C).

[0026] For evaluating the vaporization characteristic of the resulting  $\beta$ -diketonatocopper(I) complex, the thermogravimetric curve (heating rate:  $10^\circ\text{C}/\text{min.}$ , under nitrogen atmosphere) was measured. Consequently, it was found that the complex has extremely high volatility and good vaporization characteristic. Boiling point:  $140\text{-}164^\circ\text{C}$ .

## (Example 2)

[0027] Under nitrogen atmosphere, into 3.0 g of copper(I) oxide was poured 30 ml of dry dichloromethane that was fully degassed and the atmosphere of which was replaced with nitrogen to give a suspension solution. 1.72 g of 1,2-cyclononadiene was added to the solution with vigorous stirring, then 3.23 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was slowly added from a dropping funnel. After the reaction solution was stirred for 4 hours, the solution was filtered under nitrogen atmosphere, and the filtrate was concentrated under reduced pressure at room temperature to give a green liquid.

[0028] The liquid was purified through a column chromatography to give 5.63 g of (1,2-cyclononadiene) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1,2-cyclononadiene as a ligand represented by formula (7)



as an yellow solid.

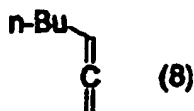
[0029] The resulting  $\beta$ -diketonatocopper(I) complex was identified with  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ .  $^1\text{H-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ) 1.38-1.77 (m, 8H), 2.06-2.24 (m, 4H), 5.26-5.32 (m, 2H), 6.10 (s, 1H).

$^{13}\text{C-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ) 23.65, 25.49, 28.44, 88.28, 90.61, 118.65 (q,  $J_{\text{C-F}}=284.1\text{Hz}$ , 2C), 173.83, 178.63 (q,  $J_{\text{C-CF}}=34.6\text{Hz}$ , 2C).

[0030] For evaluating the vaporization characteristic of the resulting  $\beta$ -diketonatocopper(I) complex, the thermogravimetric curve (heating rate:  $10^\circ\text{C}/\text{min.}$ , under nitrogen atmosphere) was measured. Consequently, the complex had a melting point of  $46.8^\circ\text{C}$  and a boiling point of  $195.6^\circ\text{C}$ .

## (Example 3)

[0031] In a similar manner as Example 2, starting from 3.0 g of copper(I) oxide, 1.30 g of 1,2-heptadiene and 3.23 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 2.82 g of (1,2-heptadiene) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1,2-heptadiene as a ligand represented by formula (8)



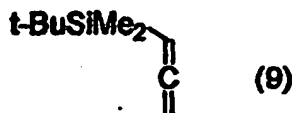
was obtained as an yellow liquid.

<sup>1</sup>H-NMR (δ, CDCl<sub>3</sub>) 0.89 (t, J=7.3Hz, 3H), 1.30-1.42 (m, 2H), 1.42-1.54 (m, 2H), 2.15-2.27 (m, 2H), 4.33-4.40 (m, 2H), 5.45-5.55 (m, 1H), 6.13 (s, 1H). <sup>13</sup>C-NMR (δ, CDCl<sub>3</sub>) 13.95, 22.46, 31.50, 31.70, 55.72, 90.76, 92.44, 117.96 (q, J<sub>C-F</sub>=283.7Hz, 2C), 165.80, 178.85 (q, J<sub>C-F</sub>=34.5Hz, 2C).

[0032] For evaluating the vaporization characteristic of the resulting β-diketonatocopper(I) complex, the thermogravimetric curve (heating rate: 10°C/min., under nitrogen atmosphere) was measured. Consequently, the complex had a boiling point of 150.0°C.

## (Example 4)

[0033] In a similar manner as Example 2, starting from 3.0 g of copper(I) oxide, 2.16 g of 1-(dimethyl-tert-butyldisilyl) allene and 3.23 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 3.47 g of [(1-(dimethyl-tert-butyldisilyl) allene)] (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1-(dimethyl-tert-butyldisilyl) allene as a ligand represented by formula (9)

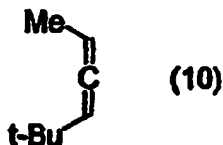


was obtained as an yellow liquid. <sup>1</sup>H-NMR (δ, CDCl<sub>3</sub>) 0.20 (s, 6H), 0.97 (s, 9H), 4.35 (d, J=4.0Hz, 2H), 4.87 (t, J=4.4Hz, 1H), 6.15 (s, 1H). <sup>13</sup>C-NMR (δ, CDCl<sub>3</sub>) 5.40, 18.72, 26.61, 55.36, 69.50, 90.93, 117.94 (q, J<sub>C-F</sub>=283.8Hz, 2C), 159.51, 178.96 (q, J<sub>C-F</sub>=34.8Hz, 2C).

[0034] For evaluating the vaporization characteristic of the resulting β-diketonatocopper(I) complex, the thermogravimetric curve (heating rate: 10°C/min., under nitrogen atmosphere) was measured. Consequently, the complex had a boiling point of 140.0°C.

## (Example 5)

[0035] In a similar manner as Example 2, starting from 3.0 g of copper(I) oxide, 1.54 g of 1-(tert-butyl)-2-methyl allene and 3.23 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1.78 g of [1-(tert-butyl)-2-methyl allene] (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1-(tert-butyl)-2-methyl allene as a ligand represented by formula (10)



was obtained as an yellow liquid. <sup>1</sup>H-NMR (δ, CDCl<sub>3</sub>) 1.18 (s, 9H), 1.89-1.98 (m, 3H), 5.30-5.40 (m, 2H), 6.11 (s,

1H).  $^{13}\text{C}$ -NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 18.42, 30.41, 36.41, 79.79, 90.77, 93.20, 117.94 (q,  $J_{\text{C-F}}=283.8\text{Hz}$ , 2C), 150.16, 178.78 (q,  $J_{\text{C-F}}=34.9\text{Hz}$ , 2C).

[0036] For evaluating the vaporization characteristic of the resulting p-diketonatocopper(I) complex, the thermogravimetric curve (heating rate:  $10^\circ\text{C}/\text{min.}$ , under nitrogen atmosphere) was measured. Consequently, the complex had a boiling point of  $147.0^\circ\text{C}$ .

(Example 6)

[0037] Under nitrogen atmosphere, into 3.0 g of copper(I) oxide was poured 30 ml of dry dichloromethane that was fully degassed and the atmosphere of which was replaced with nitrogen to give a suspension solution. 0.96 g of 1,1-dimethyl allene was added to the solution with vigorously stirring, then 3.2 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was slowly added from a dropping funnel. After the reaction solution was stirred for 12 hours, the solution was filtered under nitrogen atmosphere, and the filtrate was concentrated under reduced pressure at room temperature to give a green liquid.

[0038] The liquid was purified through a column chromatography to give 2.3 g of (1,1-dimethyl allene) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1,1-dimethyl allene as a ligand represented by formula (11).



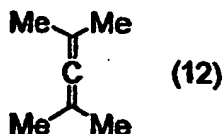
as an yellow liquid.

[0039] The resulting  $\beta$ -diketonatocopper(I) complex was identified with  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR.  $^1\text{H}$ -NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 1.96 (t,  $J=2.8\text{Hz}$ , 6H), 4.16 (t,  $J=2.8\text{Hz}$ , 2H), 6.16 (s, 1H).  $^{13}\text{C}$ -NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 22.63 (2C), 50.03, 90.24, 108.41, 117.75 (q,  $J_{\text{C-F}}=284.9\text{Hz}$ , 2C), 175.10, 178.40 (q,  $J_{\text{C-F}}=34.7\text{Hz}$ , 2C).

(Example 7)

[0040] Under nitrogen atmosphere, into 3.0 g of copper(I) oxide was poured 30 ml of dry dichloromethane that was fully degassed and the atmosphere of which was replaced with nitrogen to give a suspension solution. 1.35 g of 1,1,3,3-tetramethyl allene was added to the solution with vigorously stirring, then 3.2 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was slowly added from a dropping funnel. After the reaction solution was stirred for 12 hours, the solution was filtered under nitrogen atmosphere, and the filtrate was concentrated under reduced pressure at room temperature to give a green liquid.

[0041] The liquid was purified through a column chromatography to give 3.8 g of (1,1,3,3-tetramethyl allene) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1,1,3,3-tetramethyl allene as a ligand represented by formula (12)



as an yellow solid.

[0042] The resulting  $\beta$ -diketonatocopper(I) complex was identified with  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR.  $^1\text{H}$ -NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 2.00 (s, 12H), 6.18 (s, 2H).  $^{13}\text{C}$ -NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 24.84 (4C), 90.50 (2C), 93.25 (2C), 117.81 (q,  $J_{\text{C-F}}=285.3\text{Hz}$ , 4C), 145.33, 178.61 (q,  $J_{\text{C-F}}=34.7\text{Hz}$ , 4C).

[0043] Table 1 indicates the  $\beta$ -diketonatocopper(I) complexes (including ones synthesized in Examples described above) of the present invention synthesized according to the producing process or Examples described above along with allene compounds of their ligands (L) [formula (1)], but the present invention is not limited thereto.



Table 1

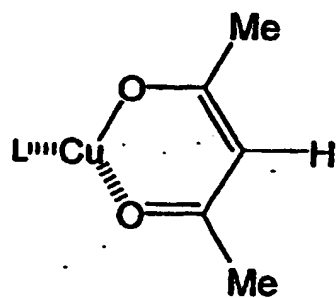
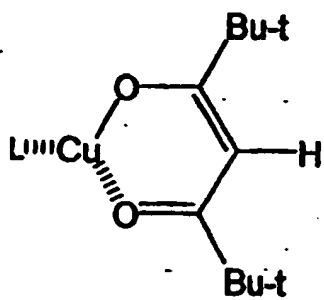
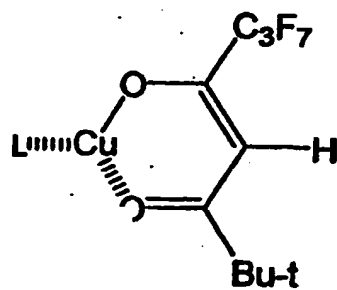
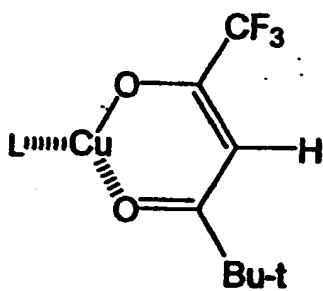
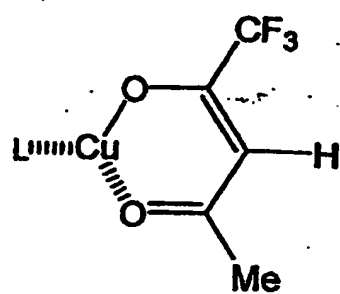
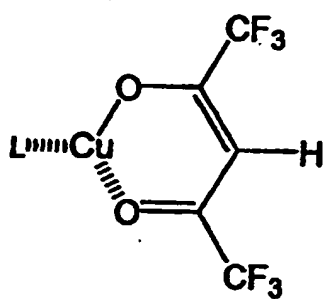
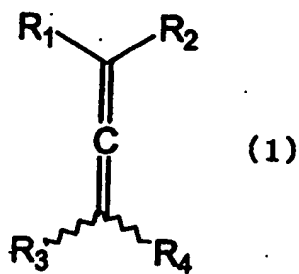


Table 1 (continued)

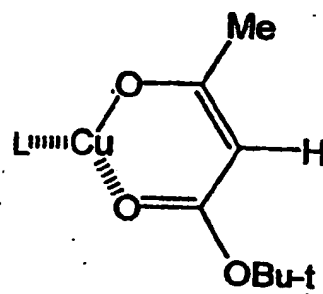
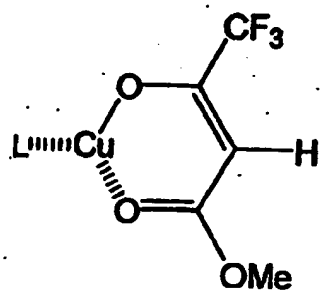


Table 1 (continued)

	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
5	H	H	H	H
10	H	Me	H	H
	H	Et	H	H
15	H	n-Pr	H	H
	H	n-Bu	H	H
	H	i-Pr	H	H
20	H	i-Bu	H	H
	H	s-Bu	H	H
25	H	t-Bu	H	H
	H	Me <sub>3</sub> Si	H	H
30	H	Et <sub>3</sub> Si	H	H
	H	n-Pr <sub>3</sub> Si	H	H
35	H	n-Bu <sub>3</sub> Si	H	H
	H	i-Pr <sub>3</sub> Si	H	H
40	H	Me <sub>2</sub> (Et)Si	H	H
	H	Me <sub>2</sub> (n-Pr)Si	H	H
	H	Me <sub>2</sub> (i-Pr)Si	H	H
45	H	Me <sub>2</sub> (t-Bu)Si	H	H
	Me	Me	H	H
50	Me	Et	H	H

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Table 1 (continued)

	$R_1$	$R_2$	$R_3$	$R_4$
5	Me	n-Pr	H	H
10	Me	n-Bu	H	H
	Me	i-Pr	H	H
15	Me	i-Bu	H	H
	Me	s-Bu	H	H
20	Me	t-Bu	H	H
	Me	Me <sub>3</sub> Si	H	H
25	Me	Et <sub>3</sub> Si	H	H
	Me	n-Pr <sub>3</sub> Si	H	H
	Me	n-Bu <sub>3</sub> Si	H	H
30	Me	i-Pr <sub>3</sub> Si	H	H
	Me	Me <sub>2</sub> (Et)Si	H	H
35	Me	Me <sub>2</sub> (n-Pr)Si	H	H
	Me	Me <sub>2</sub> (i-Pr)Si	H	H
40	Me	Me <sub>2</sub> (t-Bu)Si	H	H
	Et	Et	H	H
45	Et	n-Pr	H	H
	Et	n-Bu	H	H
50	Et	i-Pr	H	H
	Et	i-Bu	H	H

Table 1 (continued)

	$R_1$	$R_2$	$R_3$	$R_4$
5	Et	s-Bu	H	H
10	Et	t-Bu	H	H
	n-Pr	n-Pr	H	H
15	n-Pr	n-Bu	H	H
	n-Pr	i-Pr	H	H
	n-Pr	i-Bu	H	H
20	n-Pr	s-Bu	H	H
	n-Pr	t-Bu	H	H
25	n-Bu	n-Pr	H	H
	n-Bu	i-Pr	H	H
30	n-Bu	i-Bu	H	H
	n-Bu	s-Bu	H	H
35	n-Bu	t-Bu	H	H
	Me <sub>3</sub> Si	Et	H	H
	Me <sub>3</sub> Si	n-Pr	H	H
40	Me <sub>3</sub> Si	n-Bu	H	H
	Me <sub>3</sub> Si	i-Pr	H	H
45	Me <sub>3</sub> Si	i-Bu	H	H
	Me <sub>3</sub> Si	s-Bu	H	H
50	Me <sub>3</sub> Si	t-Bu	H	H

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Table 1 (continued)

$R_1$	$R_2$	$R_3$	$R_4$
$n\text{-Bu}_3\text{Si}$	Et	H	H
$n\text{-Bu}_3\text{Si}$	$n\text{-Pr}$	H	H
$n\text{-Bu}_3\text{Si}$	$n\text{-Bu}$	H	H
$n\text{-Bu}_3\text{Si}$	$i\text{-Pr}$	H	H
$n\text{-Bu}_3\text{Si}$	$i\text{-Bu}$	H	H
$n\text{-Bu}_3\text{Si}$	$s\text{-Bu}$	H	H
$n\text{-Bu}_3\text{Si}$	$t\text{-Bu}$	H	H
$\text{Me}_2(\text{t-Bu})\text{Si}$	Et	H	H
$\text{Me}_2(\text{t-Bu})\text{Si}$	$n\text{-Pr}$	H	H
$\text{Me}_2(\text{t-Bu})\text{Si}$	$n\text{-Bu}$	H	H
$\text{Me}_2(\text{t-Bu})\text{Si}$	$i\text{-Pr}$	H	H
$\text{Me}_2(\text{t-Bu})\text{Si}$	$i\text{-Bu}$	H	H
$\text{Me}_2(\text{t-Bu})\text{Si}$	$s\text{-Bu}$	H	H
$\text{Me}_2(\text{t-Bu})\text{Si}$	$t\text{-Bu}$	H	H
$\text{Me}_3\text{Si}$	$\text{Me}_3\text{Si}$	H	H
$\text{Me}_3\text{Si}$	$\text{Me}_2(\text{t-Bu})\text{Si}$	H	H
	$-(\text{CH}_2)_2-$	H	H
	$-(\text{CH}_2)_5-$	H	H

Table 1 (continued)

	<b>R<sub>1</sub></b>	<b>R<sub>2</sub></b>	<b>R<sub>3</sub></b>	<b>R<sub>4</sub></b>
5	Me	H	Me	H
10	Me	H	Et	H
	Me	H	n-Pr	H
15	Me	H	n-Bu	H
	Me	H	i-Pr	H
20	Me	H	i-Bu	H
	Me	H	s-Bu	H
	Me	H	t-Bu	H
25	Me	H	Me <sub>3</sub> Si	H
	Me	H	Et <sub>3</sub> Si	H
30	Me	H	n-Pr <sub>3</sub> Si	H
	Me	H	n-Bu <sub>3</sub> Si	H
35	Me	H	i-Pr <sub>3</sub> Si	H
	Me	H	Me <sub>2</sub> (Et)Si	H
40	Me	H	Me <sub>2</sub> (n-Pr)Si	H
	Me	H	Me <sub>2</sub> (i-Pr)Si	H
45	Me	H	Me <sub>2</sub> (t-Bu)Si	H
	Et	H	Et	H
	Et	H	n-Pr	H
50	Et	H	n-Bu	H

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Table 1 (continued)

	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
5	Et	H	i-Pr	H
10	Et	H	i-Bu	H
	Et	H	s-Bu	H
15	Et	H	t-Bu	H
	n-Pr	H	n-Pr	H
20	n-Pr	H	n-Bu	H
	n-Pr	H	i-Pr	H
	n-Pr	H	i-Bu	H
25	n-Pr	H	s-Bu	H
	n-Pr	H	t-Bu	H
30	n-Bu	H	n-Pr	H
	n-Bu	H	i-Pr	H
35	n-Bu	H	i-Bu	H
	n-Bu	H	s-Bu	H
40	n-Bu	H	t-Bu	H
	Me <sub>3</sub> Si	H	Et	H
	Me <sub>3</sub> Si	H	n-Pr	H
45	Me <sub>3</sub> Si	H	n-Bu	H
	Me <sub>3</sub> Si	H	i-Pr	H
50	Me <sub>3</sub> Si	H	i-Bu	H



Table 1 (continued)

	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
5	Me <sub>3</sub> Si	H	s-Bu	H
10	Me <sub>3</sub> Si	H	t-Bu	H
	n-Bu <sub>3</sub> Si	H	Et	H
15	n-Bu <sub>3</sub> Si	H	n-Pr	H
	n-Bu <sub>3</sub> Si	H	n-Bu	H
20	n-Bu <sub>3</sub> Si	H	i-Pr	H
	n-Bu <sub>3</sub> Si	H	i-Bu	H
25	n-Bu <sub>3</sub> Si	H	s-Bu	H
	n-Bu <sub>3</sub> Si	H	t-Bu	H
30	Me <sub>2</sub> (t-Bu)Si	H	Et	H
	Me <sub>2</sub> (t-Bu)Si	H	n-Pr	H
	Me <sub>2</sub> (t-Bu)Si	H	n-Bu	H
35	Me <sub>2</sub> (t-Bu)Si	H	i-Pr	H
	Me <sub>2</sub> (t-Bu)Si	H	i-Bu	H
40	Me <sub>2</sub> (t-Bu)Si	H	s-Bu	H
	Me <sub>2</sub> (t-Bu)Si	H	t-Bu	H
45	Me <sub>3</sub> Si	H	Me <sub>3</sub> Si	H
	Me <sub>3</sub> Si	H	Me <sub>2</sub> (t-Bu)Si	H
50	H	-(CH <sub>2</sub> ) <sub>6</sub> -		H
	H	-(CH <sub>2</sub> ) <sub>7</sub> -		H

Table 1 (continued)

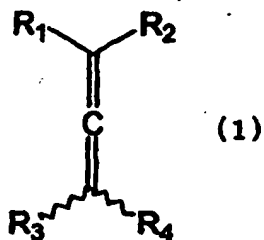
$R_1$	$R_2$	$R_3$	$R_4$
Me	Me	Me	H
Me	Et	Me	H
Me	Et	i-Bu	H
Me	i-Bu	Me	H
Me	Me	Me <sub>3</sub> Si	H
Me	Me <sub>3</sub> Si	n-Bu	H
n-Bu	Me <sub>3</sub> Si	Me	H
Me	Me <sub>3</sub> Si	Me <sub>3</sub> Si	H
Me <sub>3</sub> Si	Me <sub>3</sub> Si	Me <sub>3</sub> Si	H
	-(CH <sub>2</sub> ) <sub>4</sub> -	Me	H
	-(CH <sub>2</sub> ) <sub>5</sub> -	Me	H
Me		-(CH <sub>2</sub> ) <sub>6</sub> -	H
Me	Me	Me	Me
Me	n-Bu	Me	Me
Me	Me <sub>3</sub> Si	Me	n-Pr
n-Bu	Me <sub>3</sub> Si	Me	Me
Me	Me <sub>3</sub> Si	n-Bu	n-Bu
Me <sub>3</sub> Si	Me <sub>3</sub> Si	Me <sub>3</sub> Si	Me <sub>3</sub> Si
	-(CH <sub>2</sub> ) <sub>5</sub> -	Me	n-Pr

## Industrial Applicability

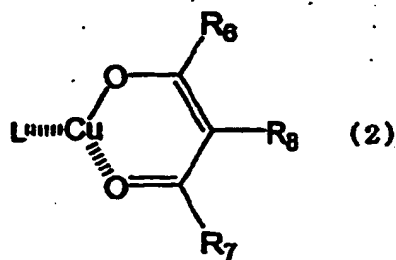
[0044] The present invention provides novel  $\beta$ -diketonatocopper(I) complexes and processes for producing the same. The  $\beta$ -diketonatocopper(I) complexes according to the present invention are useful as compounds for forming a thin copper film by MOCVD method.

## Claims

1. A  $\beta$ -diketonatocopper(I) complex which contains as a ligand (L) an allene compound of formula (1)

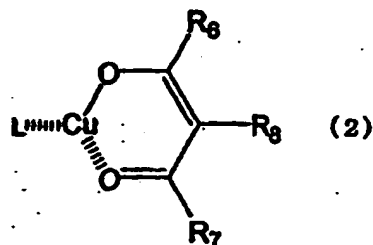


wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represents hydrogen,  $C_{1-4}$  alkyl or  $(R_5)_3Si$ -, or  $R_1$  and  $R_2$ , together with the carbon atom bonding them, may form 3- to 6-member ring, or  $R_2$  and  $R_3$ , together with the allene bond group bonding them, may form 8- to 10-member ring,  $R_5$ s may be the same or different and independently of one another represent linear or branched  $C_{1-4}$  alkyl, and which is represented by formula (2)

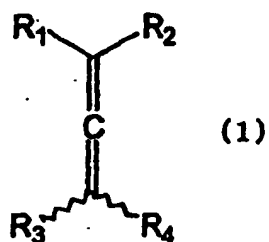


wherein,  $R_6$  and  $R_7$  may be the same or different and each represents linear or branched  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, or linear or branched  $C_{1-4}$  fluoroalkyl,  $R_8$  represents hydrogen or fluorine, and L represents the allene compound of formula (1).

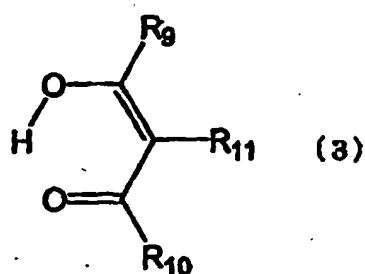
2. A process for producing a  $\beta$ -diketonatocopper(I) complex represented by formula (2)



wherein,  $R_6$  and  $R_7$  may be the same or different and each represents linear or branched  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, or linear or branched  $C_{1-4}$  fluoroalkyl,  $R_8$  represents hydrogen or fluorine, and L represents the allene compound of formula (1), characterized in that the process comprises reacting an allene compound of formula (1)



15 wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represents hydrogen,  $C_{1-4}$  alkyl or  $(R_5)_3Si-$ , or  $R_1$  and  $R_2$ , together with the carbon atom bonding them, may form 3- to 6-member ring, or  $R_2$  and  $R_3$ , together with the allene bond group bonding them, may form 8- to 10-member ring,  $R_5$ s may be the same or different and independently of one another represent linear or branched  $C_{1-4}$  alkyl, with an enol compound of formula (3)



30 wherein  $R_9$  and  $R_{10}$  may be the same or different and each represents linear or branched  $C_{1-4}$  alkyl,  $C_{1-4}$  alkoxy, or linear or branched  $C_{1-4}$  fluoroalkyl,  $R_{11}$  represents hydrogen or fluorine in the presence of a copper(I) compound.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/01956

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl. <sup>7</sup> C07C49/92, 45/77, 11/14, 13/02, C07F7/08 //C07F1/08, C23C16/18		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>7</sup> C07C49/92, 45/77, 11/14, 13/02, C07F7/08, C07F1/08, C23C16/18		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, 498269, A2 (AIR PRODUCTS AND CHEMICALS, INC.), 12 August, 1992 (12.08.92) & US, 5085731, A & JP, 5-59551, A & KR, 9411709, B1	1, 2
A	EP, 533070, A2 (AIR PRODUCTS AND CHEMICALS, INC.), 24 March, 1993 (24.03.93) & US, 5187300, A & JP, 5-202476, A & KR, 9504895, B1	1, 2
A	EP, 493754, A1 (AIR PRODUCTS AND CHEMICALS, INC.), 08 July, 1992 (08.07.92) & US, 5098516, A & JP, 4-318170, A & KR, 9405327, B1 & IB, 73257, B	1, 2
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 04 April, 2001 (04.04.01)		Date of mailing of the international search report 17 April, 2001 (17.04.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)